Recent advances in green synthesis of carbon dots for heavy metal ion sensing

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Abstract. In recent years, the field of green synthesis for carbon dots has seen significant advancements in the development of materials for heavy metal ion sensing applications. A variety of eco-friendly and sustainable approaches have been explored to synthesize carbon dots (CDs) with enhanced sensing properties. These materials have shown great promise in detecting heavy metal ions due to their high sensitivity, selectivity, and low detection limits One of the key advancements in this area is the utilization of natural sources such as biomass, organic waste, and plant extracts as precursors for the synthesis of CDs. These green precursors not only contribute to the sustainable nature of the synthesis process but also result in the production of carbon dots with unique surface chemistry and optical properties. In addition to the synthesis and functionalization strategies, the understanding of the underlying mechanisms governing the interaction between CDs and heavy metal ions has advanced significantly. This improved understanding has facilitated the design of CDs with tailored sensing capabilities and improved overall performance. Overall, the recent progress in the green synthesis of CDs for heavy metal ion sensing holds great promise for the development of cost-effective, environmentally friendly, and high-performance sensing platforms with potential applications in environmental monitoring, industrial safety, and healthcare diagnostics.

1 Introduction

The presence of toxic metal ions pose a significant threat to human health as well as the environment[1]. Among all metal pollutants mercury, lead, chromium, cadmium, and arsenic are most contributed pollutants found in our environment causing several diseases including brain damage, cancer, cardiovascular diseases, liver and bones damage and neurological

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The heavy metal can be naturally occurring or can be produced due to human activities, it is present in our environment in trace amount due to which it is difficult to mitigate. The density of heavy metals ions are atleast five time greater than density of water [2].

To control the problem of sudden risen pollution due to heavy metal ions is a great area of research nowadays. Consequently, researchers try to find an effective and economical way for the detection of these toxins to eliminate their impact on human health and the environment. Nanotechnology is introduced in which nanoparticles having small size and high surface-to-volume ratio are taken into consideration. NMs also good sensors and catalysis characteristics, which are used in different fields [3–5]. CDs shows best result as it exhibits excellent properties towards photoluminescence [6,7]. Carbon dots are having size less than 10nm were reported first time in 2004 exhibits various properties including (i)thermal stability, (ii)less toxic, (iii) soluble in water, (iv) photoluminescence and most importantly (v)excellent quantum yield which make them suitable for sensing application. In past few years several methods consisting of laser ablation, microwave-assisted, pyrolysis, and solvothermal have been involved in the synthesis of CDs. However, the problem with these methods is the high toxicity and need of additional expensive reagents as a precursor, still resulting in low yield and low stability. There are no such benefits as these approaches have their own disadvantages due to the use of hazardous chemicals as precursors. Also, we aimed to investigate the sensing of toxins from our environment for sustainable development goals from one side and using hazardous chemicals as precursors from the other side as these are expensive and exhibit low quantum yield. Therefore, to tackle the limitations of conventional methods for the synthesis of NPs, new technology green approach is introduced [8–10]. In this approach , biogenic material is utilized for the synthesis of CDs for sensing of heavy metal ions following green chemistry principles as biogenic materials are cost-effective, readily available, high sensitivity and environmentally friendly for the sensing of heavy metal ions [11,12].

According to the green chemistry principles, a hydrothermal method using biogenic materials such as Volvariella volvacea, beetroot, Ocimum sanctum, coffee powder, Lantana camara berries, Mushroom, table sugar[13], camphor, lotus root, prawn shells, murraya koenigii leaves, Borassus flabellifer flowers[14], Eleusine corcana, Manihot esculenta, precursors for carbon dot synthesis must follows the green chemistry principles as described in Fig. 1.

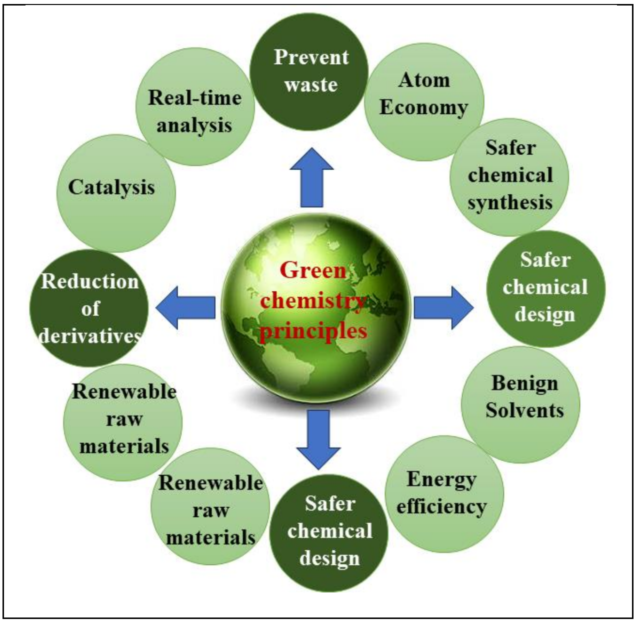

Fig. 1. Green chemistry principles for the minimization of toxic solvents.

2 Green Synthesis of CDs for detection of heavy metal ions and its importance

CDs are synthesized by using biogenic materials in which natural resources act as precursors. It is simple, cost-effective, readily available, environmentally friendly approach contributes toward sustainable development goals. Industrial activities, fossil fuel combustion, mining and smelting, agricultural waste, natural processes, wastewater discharges are some primary sources that release heavy metal pollutants into the environment. It impacts the aquatic and human life and pollutes the environment [15,16]. To control the increase in contamination of toxic pollutants in our environment, usage of natural sources play crucial role. The biogenic material also enhance the selectivity, sensitivity and detection limit of metal ions. For instance, *Nazanin and his coworkers* utilize beetroot as biogenic material for the synthesis of photoluminescent carbon dot for efficient sensing of Pd^{2+}[17]. The size, shape of CDs affects the band gap as when functional groups are increasing on the surface of CDs, a large no. of hydroxy groups localized to form electronic states under π*. The presence of extra functional group increases the gap between n-π* levels. Also, *Navneet et.al*. synthesized banana juice extracted fluorescent CDs for selective detection of Cu^{2+} ions[18]. *Bilgehan et. al*. investigated fluorescent CDs derived from Fortunella margarita for sensing of Fe3+ ions[19]. In this way all metal ions can be easily detected using green synthesis method. Various resources which release heavy metal ions and its adverse effects explains on the basis of schematic representation in Fig 2.

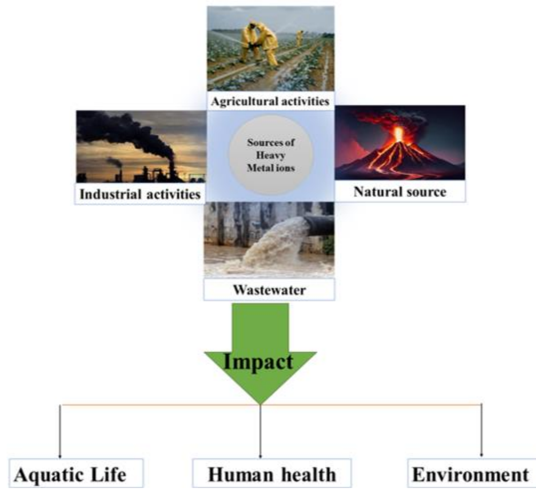

Fig 2. Various sources responsible for the release of heavy metal ions.

3 Role of CDs in heavy metal detection

The various functional groups are present on the surface of CDs which selectively bind the heavy metal ion according to the ligand interaction with different metals. The presence of functional groups on the surface of CDs enhances the selectivity towards the investigated metal ion. Metal ion can be even detected if present in trance amount due to high selectivity of CDs. The photoluminescent CDs exhibits quenching mechanism, it emits fluorescence when excited by external light source. When heavy metal solution is added into the photoluminescent CDs, it interacts with CDs and quenches the emission of CDs by electron energy transfer. In addition, the optical properties of CDs enhance the selectivity and sensitivity of sensors towards the detection of heavy metal ions [20]. The schematic representation is illustrated in Fig 3 to explain how the presence of functional groups on the surface of CDs affects the metal ions. We will discuss the CDs-based sensor for the detection of reported metal ions, discussed in the following sections.

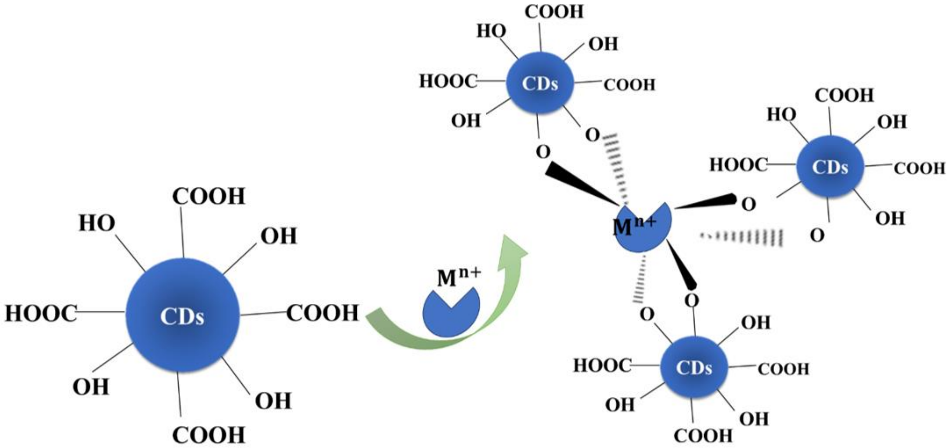

Fig. 3. Schematic representation of functional group present on CDs with metal ions(M^{n+})

3.1 CDs-based sensor for the detection of Mercury (Hg) ions

Mercury ion is one of the major contaminants due to high toxicity and is responsible for human disorders, and brain kidney damage. It exists in three forms of matter with varying toxicity and exists with different oxidation states of +1 and +2. It is therefore critical to design sensitive and selective sensors that detect mercury ions even at extremely low concentrations. Green carbon sources were used to manufacture CQDs for Hg^{2+} ion detection. However, adding them to CQDs caused fluorescence quenching. For instance, *Daraksha Bano et.al*. synthesized fluorescent CDs using tamarindus indica extract for the detection of Hg^{2+} ions. The study states that the synthesized CDs act as turn-on sensors for the detection of Hg^{2+}[21]. Also, *Aschalew Tadess et. al*. synthesized N-doped CDs derived from citrus lemon juice as a precursor for the sensing of Hg^{2+}[22]. Also,*Jing Yu et. al*. synthesized CDs using Jinhua bergamot for sensing of Hg^{2+} and Fe^{3+}[23].

3.2 CDs-based sensor for the detection of lead (Pb) ions

Lead is a naturally occurring bluish-gray metal present in small amounts in the earth's crust. Although lead occurs naturally in the environment due to anthropogenic activities such as fossil fuel burning, mining, and manufacturing contributes to the release of high concentrations. Lead had previously been added to gasoline as an anti-knock agent, resulting in wide accumulation in the atmosphere. Although leaded gasoline has been phased out in many economies, persistent pollution still exists in soils and deposits. Pb serves numerous distinct commercial, agricultural, and domestic applications due to which it is released in high amounts in the environment.

Lead (Pb) is a hazardous heavy metal that deposits in many tissues, including the blood, bones, and organs so there is an urgent need for the detection of Pb^{2+}. Because of the serious health concerns associated with lead exposure, there is an urgent need to detect and monitor lead levels in the environment, drinking water, food, and biological samples. For instance, *Agents T. Boobalan et. al.,* synthesized CDs for the detection of Pb^{2+} metal ions using a biogenic material mushroom[24]. Also, *Rajkumar Bandi et.al.* synthesized N-doped CDs derived from natural precursor Lantana camara berries for the sensing of Pb^{2+}[25].

3.3 CDs-based sensor for the detection of chromium ions

Chromium (Cr) accumulation in body organs has been linked to significant health risks. The introduction of Cr metal ions in the environment leads to many diseases including respiratory issues, lung cancer, and liver damage it may negatively affect bronchial epithelial cells by altering apoptosis-related and energy metabolism-associated proteins. Cr exists in its two most common oxidation states chromium(III) and chromium(VI) possess threats to human life. Due to industrial processes and miling activities, tons of chromium metal particles are released into water and air which disturb the ecosystem so there is a sudden need to control such activities and detect the presence of it. For instance, *Lan Xia et. al*. synthesized Chimonanthus praecox-derived CDs for the sensing of Cr^{4+} ions. *Shipeng Wang et. al.* investigated photoluminescent N, S doped CDs sensor derived from the grapefruit extract for sensing of Cr metal ions[26]. *Roshni et al*. synthesized CDs derived from groundnuts for sensing Cr(VI)ions[27]. *Yuanyuan Song et. al.* use wool keratin for the synthesis of fluorescent CDs. In this study as prepared CDs are used to detect the presence of Cr ions[28].

3.4 CDs-based sensor for the detection of copper ions

Copper (Cu) is a necessary trace element, but present in excessive amount can be hazardous. It commonly exhibits two oxidation states: +1 and +2, which are referred to as cuprous (Cu+) and cupric (Cu^{2+}) toxic to environment causes symptoms such as nausea, vomiting, diarrhea, abdominal pain, liver damage, and kidney damage. Copper can be highly toxic to aquatic organisms such as fish, invertebrates, and aquatic plants. Although copper is an essential metal for humans but prolonged exposure can have adverse health effects. Industrial exposure to copper dust or fumes in industries such as mining, smelting, and metalworking can cause respiratory problems. Attempts have been made to minimize copper pollution involve implementing chemical release rules, encouraging the use of less harmful pesticides in agriculture, upgrading wastewater treatment technologies, and raising knowledge about proper metal-product disposal processes. Furthermore, soil and water remediation procedures may be employed to eliminate existing copper contamination. The great efforts have been taken for the detection and removal of copper ions. *Navneet* and his coworkers synthesized fluorescent CDs for the sensing of copper ions derived from banana juice extraction[18]. Also, *Yingshuai Liu et. al.* synthesized CNDs from biogenic material bamboo leaves for the sensing of copper(II)ions[29]. Also, *Bipin rooj et. al.* synthesized CQDs derived from Polianthes tuberose for the detection of Cu(II) ions[30].

Table 1. Various resources for the synthesis of CDs for heavy metal ion sensing

Sr. No.	Metal ions	Method	Precursor	Quantum yield	LOD	Reference
1.	Fe^{3+} and Pb^{2+}	Hydrothermal	Volvariella volvacea mushroom	11.5%.	12 and 16 nM	[1]
2.	Pd^{2+}	Hydrothermal	Red beetroot	27.6%	33 nM	[17]
3.	Pb^{2+}	Hydrothermal	Ocimum sanctum	9.3%	0.59 nM	[31]
4.	Cu^{2+} and Pb^{2+}	pyrolysis	coffee	-	0.447 mg/L And 1.358μ g/L	[32]
5.	Pb^{2+}	Green method	bovine serum albumin	-	5.05 μM	[33]
6.	Hg^{2+}	microwave	Lotus root	19.0%	18.7 nM	[34]
7.	Fe^{3+}	Green method	Borassus flabellifer	11.73%	10 nM	[14]
8.	$Cd^{2+}$and Hg^{2+}	Green method	camphor	21.16%	NM	[35]
9.	Cu^{2+}	Hydrothermal method	bamboo leaves	7.1%	115 nM	[29]
10.	Fe^{3+}	Hydrothermal method	Fortunella margarita	0.08%	0.70 μM.	[19]

11.	Cu^{2+}	Hydrothermal	Banana juice	32%	0.3 µg mL^{-1}	[18]
12.	Hg^{2+}	Hydrothermal	Tamarindus indica	46.6 %	6nM	[21]
13.	Hg^{2+}	Hydrothermal	Citrus lemon	31%	5.3 nM	[22]
14.	Hg^{2+} and Fe^{3+}	Hydrothermal	Jinhua bergamot	50.78%	5.5 nM (Hg2+) and 0.075 µM	[23]
15.	Pb^{2+}	Hydrothermal	Mushroom	-	58.63 µM	[24]
16.	Pb^{2+}	Green synthesis	Vigna radiate and Allium cepa	52%	0.18 nM	[36]
17.	Fe^{3+}	Thermal pyrolysis	borassus flabellifer	13.97%	10nM	[14]
18.	Cr(IV)	Hydrothermal	Grapefruit juice	84.93%	0.155 µM	[26]
19.	Cr(IV)	Hydrothermal	Groundnuts	17.6%	0.1 mg/L	[37]
20.	Cu^{2+}	Green synthesis	Prawn shellls	9%	5nM	[38]
21.	Cu^{2+}, Fe^{2+}	Carbonization	Polianthes tuberose L. Petals	3%	200nM	[30]
22.	Cu^{2+}	Hydrothermal	Ganoderma lucidum bran	4.6%	0.74 µmol L^{-1}	[39]
23.	Fe^{2+}	Hydrothermal	Betel leaves	4.21%	0.11µM	[40]
24.	Cr^{6+} and Fe^{3+}	Hydrothermal	Wool keratin	8%	0.014 µM	[28]
25.	Pb2+	Hydrothermal	watermelon juice	8%	190 pM	[41]
26.	Pb2+	Green synthesis	Lantana camara berries	33.15%	9.64 nM	[25]

4 Conclusion and Future Perspectives

In conclusion, the green synthesis of CDs for sensing of metal ions holds great potential in environment monitoring and remediation efforts. By utilizing biogenic materials for the synthesis of CDs demonstrate potential for widespread applicability in detecting and monitoring metal ions in diverse environmental and industrial areas. Researchers have a keen interest now a days to synthesize NPs which uses no harmful chemicals as precursor. In this review, we discussed about the green synthesis of CDs for sensing of heavy metal ions. The unique optical properties of carbon dots make them highly effective for detecting a wide range of metal ions with high sensitivity and selectivity. It is an excellent approach towards circular economy and sustainable development goals. Furthermore, due to the unique properties of CDs including photoluminescence, surface functionalization contribute deeper understanding of their potential as highly sensitive and selective metal ion sensors. The ability of CDs to exhibits different fluorescent colors in the presence of specific metal ions further increases their versatility and utility in environmental applications.In addition, the green synthesis of CDs present an innovative and promising approach for the development of efficient and sustainable metal ion detection. As research in this field continues to advance,the practical application of these CDs in real-world scenarios holds tremendous potential for addressing environmental and public health concerns related to metal ion contamination. Overall the green synthesis of CDs hold great promise for the future of metal ion sensing.

Green, cost-effective, and sustainable methods for the detection and removal of heavy metal ions from water sources are becoming increasingly crucial due to release of harmful toxins into the environment. As the demand for eco-friendly and sustainable methods continues to grow, the development of innovative approaches for synthesizing carbon dots with minimal environmental impact is imperative. One potential direction for future research is the exploration of novel precursors and reaction conditions that can yield carbon dots with enhanced properties for heavy metal ion detection. This could involve the use of unconventional carbon sources or the incorporation of specific functional groups to tailor the chemical and optical characteristics of the carbon dots. Furthermore, the integration of carbon dots into advanced sensing platforms, such as wearable devices presents an exciting avenue for translating green synthesis strategies into practical, real-world applications. By harnessing the unique photoluminescent and surface chemistry properties of carbon dots, researchers can contribute to the development of highly sensitive and selective detection technologies for heavy metal ions in diverse sample matrices. In addition, the scalability and cost-effectiveness of green synthesis methods will be critical factors in the widespread adoption of carbon dots for heavy metal ion detection. As such, future research efforts may focus on optimizing synthetic protocols to enable large-scale production of carbon dots while minimizing resource consumption and waste generation.

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